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(54) Title: STORAGE-STABLE FOAMABLE COMPOSITIONS

(57) **Abstract:** Structural foams useful for reinforcing hollow parts of vehicles and the like are obtained by heating thermosettable compositions based on epoxy resins which contain blowing agents and boron trihalide amine adduct curatives. The use of such curatives enables the formulation of thermosettable compositions which are storage stable and capable of being processed at moderately elevated temperatures without deterioration. Activation of the thermosettable compositions can nonetheless be accomplished within a short period of time at relatively low temperature (120°C to 135°C).

STORAGE-STABLE FOAMABLE COMPOSITIONS

BACKGROUND OF THE INVENTIONField of the Invention

5 The invention pertains to storage-stable foamable compositions based on epoxy resins. More specifically, particular curing accelerators are utilized to obtain one-component thermosettable compositions which exhibit improved stability both at room temperature and at moderately elevated processing temperatures over prolonged periods of time, yet which can be quickly activated at
10 surprisingly low temperatures to provide foams capable of strengthening and stiffening hollow metal parts and the like.

Discussion of the Related Art

 It is known that a number of industries, e.g., the automobile industry, require parts that are both strong and light-weight. One way to achieve this
15 balance between strength and minimal weight utilizes hollow metal parts. However, hollow metal parts are easily distorted. Accordingly, it is also known that the presence of structural foam in the cavities of the hollow parts can improve the strength and stiffness of such parts. Typically, a foam precursor composition is placed during vehicle assembly in the portion of the hollow part where
20 reinforcement is desired, either by pumping or by means of a carrier or support inserted into the hollow part. The composition is formulated to foam and cure when the vehicle is thereafter placed in a paint cure oven.

 Generally, such foamable compositions comprise a thermosettable resin such as an epoxy resin, a blowing agent and a filler. Preferably, these foams
25 have a density of about 20-40 lb/ft³ (about 0.30-0.65 g/cc) and are able to withstand heat in excess of 175°C., more preferably in excess of 200°C. Optional ingredients include accelerators, curing agents, processing aids, stabilizers, colorants, and UV absorbers. Foamable thermosettable compositions such as, e.g., TEROCORE® (a product of Henkel Surface Technologies), are now used in
30 a variety of industries.

 One recurrent problem with many of the one-part structural foam formulations of this type that have been developed to date has been their relatively short shelf-life.

Ideally, the components of such formulations once combined together should remain stable and unreacted under the conditions normally encountered during storage and shipment. It would be highly desirable for the properties of the formulations to be unchanged when stored at temperatures at or somewhat above room temperature over a several week or several month period. Unfortunately, certain of the presently available one part thermosettable compositions useful for producing structural foams tend to partially expand and cure at a temperature of 55°C (a temperature which storage facilities and transportation means frequently exceed during the summer months or in warm climates) within 24 hours. Merely lowering the amount of curative is not the solution to the problem, since this will typically adversely affect the ability to cure and foam the composition when desired within commercially acceptable temperature and time limits.

One solution to this problem is described in WO 00/12595, corresponding to U.S. Ser. No. 09/260,421, filed March 1, 1999 (incorporated herein by reference in its entirety). The use of amine-epoxy adduct curatives in combination with azodicarbonamide blowing agent provides foamable thermosettable compositions having improved stability at ambient or somewhat elevated temperatures. However, it has been found that the amine-epoxy adduct curatives suggested in WO 00/12595 must be heated to a relatively high temperature (e.g., at least about 150°C) to achieve full expansion and curing. Although paint cure ovens used in vehicle production typically are maintained at an average temperature which is sufficient to achieve the desired activation, certain regions of such ovens may be significantly cooler. For example, a thermosettable composition in accordance with WO 00/12595 which has been introduced into a hollow section near the base of a vehicle (such as, for example, a lower rail section) may not completely foam and cure within the time the vehicle remains in the paint cure oven since the oven temperature in the region where such hollow section is located may be only 120°C to 135°C.

It would therefore be highly desirable to develop a thermosettable composition that not only remains stable during prolonged storage at temperatures up to 55°C but is capable of being foamed and cured within a short period of time upon being exposed to a temperature in the range of about 120°C to about 135°C.

Additionally, it would be advantageous if such compositions also were stable at 80°C for at least 24 hours, as in certain applications the composition may need to be processed at such temperatures (for example, where the composition is to be applied by pumping or where the composition is to be molded or extruded and its viscosity at ambient temperatures is excessive).

SUMMARY OF THE INVENTION

It has been discovered that the shelf-life problems encountered with conventional thermosettable compositions used to prepare structural reinforcement foams may be effectively alleviated through the use of boron halide amine adducts (especially boron trichloride amine adducts) as curatives. At the same time, however, thermosettable compositions containing such adducts are able to be quickly cured and foamed upon heating to a temperature which is only moderately elevated (120°C to 135°C). This combination of features was unexpected, as acceptable storage stability in such compositions at 55°C can ordinarily only be achieved through the use of curatives such as amine-epoxy adducts which are activated at temperatures of 150°C or higher.

The present invention thus provides thermosettable compositions comprising:

- (a) at least one epoxy resin;
- (b) at least one blowing agent;
- (c) at least one curative which is a boron halide amine adduct (preferably, a boron trichloride amine adduct);
- (d) hollow glass microspheres; and
- (e) at least one thixotropic agent

wherein said thermosettable composition is stable at 55°C for a period of at least 1 week and at 80°C for a period of at least 1 day and is curable and foamable within about 10 minutes upon being exposed a temperature in the range of about 120°C to about 135°C. In the context of this invention, the term "stable" means that the viscosity and the specific gravity do not change by more than 20% from their initial values over the applicable time period.

DETAILED DESCRIPTION OF THE INVENTION

The thermosettable compositions of the present invention are cured using amine adducts (also referred to as "complexes") of boron trihalides such as boron trichloride. It is critical to use the boron trihalides in adduct form, as uncomplexed boron trichloride, for example, is a corrosive gas at room temperature which would be difficult to contain within the thermosettable composition during storage and handling. Additionally, it has been found that boron trichloride amine adducts rather than boron trifluoride amine adducts are greatly preferred for use in the present invention due to the tendency for the latter substances to initiate more pronounced exotherms in thermosettable compositions than the boron trichloride analogues. This problem is especially severe when a large mass of thermosettable composition is being utilized; burning, charring and non-uniform expansion of the thermosettable composition takes place, creating large holes or voids in the foam produced. Critical physical properties such as modulus and compression strength are thereby adversely affected.

Preferably, boron trihalide amine adducts are the only curatives present in the thermosettable compositions. However, in certain embodiments, minor amounts of other curatives may also be utilized in combination with the boron trihalide amine adducts provided such additional curatives do not interfere with the desired storage and processing stability of the thermosettable composition. For example, about 0.05 to about 1.0 weight % of a guanidine such as dicyandiamide may be incorporated in the thermosettable composition. However, the post-cure odor may be adversely affected by the presence of curatives other than boron trihalide amine adducts.

The amount of boron trihalide amine adduct must be selected to be sufficient to initiate curing and cross-linking of the thermosettable composition within a preselected period of time (typically, within about 10 minutes) when exposed to a temperature within the range of from about 120°C to about 135°C. The precise amount used is otherwise not believed to be critical and will vary somewhat depending upon a number of factors, including, for example, the reactivity of the particular epoxy resin(s) and other components present in the thermosettable composition. Typically, however, the concentration of boron

trihalide amine adduct will vary from about 0.2 to about 5 weight % of the thermosettable composition (more preferably, about 0.5 to about 3.5 weight %).

Boron trihalide amine adducts suitable for use in the present invention are described in U.S. Pat. No. 3,395,121, incorporated herein by reference in its entirety. Such adducts are also available commercially from companies such as CIBA Specialty Chemicals, Leepoxy Plastics, Inc. and CVC Specialty Chemicals, Inc. The amine component may be a primary, secondary, or tertiary amine; combinations of different amines may also be employed. The amine may be substituted with aliphatic, and/or aryl, and/or arylalkyl groups and may be a heterocyclic compound. The amine component should be selected to impart the desired degree of storage and processing stability as well as the desired activation temperature and curing time to the thermosettable composition.

Any of the thermosettable resins having an average of more than one (preferably about two or more) epoxy groups per molecule known or referred to in the art may be utilized as the epoxy resin component of the present invention. Epoxy resins are described, for example, in the chapter entitled "Epoxy Resins" in the Second Edition of the Encyclopedia of Polymer Science and Engineering, Volume 6, pp. 322-382 (1986). Exemplary epoxy resins include polyglycidyl ethers obtained by reacting polyhydric phenols such as bisphenol A, bisphenol F, bisphenol AD, catechol, resorcinol, or polyhydric alcohols such as glycerin and polyethylene glycol with haloepoxides such as epichlorohydrin; glycidylether esters obtained by reacting hydroxycarboxylic acids such as p-hydroxybenzoic acid or beta-hydroxy naphthoic acid with epichlorohydrin or the like; polyglycidyl esters obtained by reacting polycarboxylic acids such as phthalic acid, tetrahydrophthalic acid or terephthalic acid with epichlorohydrin or the like; epoxidated phenolic-novalac resins (sometimes also referred to as polyglycidyl ethers of phenolic novolac compounds); epoxidated polyolefins; glycidylated aminoalcohol compounds and aminophenol compounds, hydantoin diepoxides and urethane-modified epoxy resins. Mixtures of epoxy resins may be used if so desired; for example, mixtures of liquid (at room temperature), semi-solid, and/or solid epoxy resins can be employed. Any of the epoxy resins available from commercial sources are suitable for use in the present invention. Preferably, the epoxy resin has an epoxide equivalent molecular weight of from about 150 to about 1000. The use of epoxy resins based on glycidyl ethers of bisphenol A is

especially advantageous. Such epoxy resins are commercially produced by the reaction of bisphenol A with epichlorohydrin and thus are typically mixtures of molecules having somewhat different degrees of condensation. The epoxy resin preferably contains an average of about 2 epoxy groups per molecule and should be selected so as to provide the desired combination of properties in both the thermosettable composition and the final cured thermoset and composite prepared therefrom.

Selection of the blowing agent or blowing agents to be used in the present invention is not believed to be particularly critical, although chemical blowing agents and/or encapsulated physical blowing agents rather than non-encapsulated physical blowing agents should be used if a storage-stable, ready-to-use one-part composition is desired. The blowing agent should preferably be substantially inert at normal storage temperatures (e.g., up to about 55°C) but capable of being activated when exposed to temperatures within the range of about 120°C to about 135°C. Any of the chemical blowing agents known in the art may be employed, with azodicarbonamide (also sometimes referred to as 1,1'-azobisformamide) and sulfonyl hydrazides providing particularly good performance. In one embodiment of the invention, azodicarbonamide is used as the predominate or, more preferably, sole blowing agent; mixtures with sulfonylhydrazides may be desirable for certain purposes, however. Azodicarbonamide is available from a number of commercial sources; for example, it is sold under the trademark UNICELL by Dong Jin Chemical of South Korea and under the CELOGEN trademark by Uniroyal Chemical. "Activated" or "modified" forms of azodicarbonamide may be used to advantage. Suitable sulfonylhydrazide blowing agents include, but are not limited to, p,p'-oxybis (benzenesulfonylhydrazide) (sold by Uniroyal Chemical under the trademark CELOGEN OT), p-toluenesulfonylhydrazide (sold by Uniroyal Chemical under the trademark CELOGEN TSH) and the like. The particle size of the blowing agent may be adjusted so as to provide the desired foaming characteristics in the cured foam. Smaller particle sizes, for example, tend to provide foams having more uniform cell structure.

Expandable thermoplastic resin microspheres (which can comprise, for example, volatile physical blowing agents such as hydrocarbons or halocarbons encapsulated in thermoplastic shells) may also be employed to render the

thermosettable composition foamable. Particularly preferred expandable microspheres are available from Akzo Nobel AB under the trademark EXPANCEL.

In some formulations, it may be desirable to also use a blowing agent activator or accelerator so as to lower the temperature at which release of gas from the blowing agent takes place. Suitable blowing agent activators include, but are not limited to, ureas (such as the surface-coated, oil-treated urea sold by Uniroyal Chemicals under the trademark BIKOT), polyols, organic acids, amines, and lead, zinc, tin, calcium and cadmium oxides and salts (including carboxylic acid salts). Typically, from about 0.1% to about 2% blowing agent activator based on the weight of the thermosettable composition is employed, although the optimum amount will of course vary depending upon the activator/accelerator selected, the amount of blowing agent, cure temperature and other variables. Excess activator should not be used since the storage and processing stability may thereby be adversely affected.

Hollow glass microspheres are added to the thermosettable composition to reduce the density and weight of the resulting thermoset while maintaining good strength and stiffness. Commercially available hollow glass microspheres (sometimes also referred to as glass microballoons or microbubbles) include the materials sold by Minnesota Mining & Manufacturing under the trademark SCOTCHLITE, with suitable grades including those available under the designations B38, C15, K20 and VS 5500. The glass microspheres preferably have diameters in the range of from about 5 to 200 micrometers (preferably, no greater than 70 micrometers). The crush strength of the hollow glass microspheres may be selected in accordance with the desired characteristics of the cured thermoset or composite containing such thermoset. Preferably, the crush strength is at least about 200 Kg/cm² to permit processing of the thermosettable composition by pumping or the like without crushing the microspheres.

Other types of fillers may also optionally be present in the thermosettable composition. Glass fiber is a preferred type of filler, since it helps increase the strength and stiffness of the thermoset. The glass fiber may be chopped, milled or in other suitable physical form. Any of the conventional organic or inorganic fillers known in the thermosettable resin art may be used including, for example, fibers other than glass fibers (e.g., wollastonite fibers, carbon fibers, ceramic fibers,

polyaramid fibers), calcium oxide, wollastonite (including high aspect ratio wollastonite, which chemically is comprised of calcium silicate), alumina, mica, talc, zinc oxide, clays, sand, metals (e.g., aluminum powder), microspheres and macrospheres comprised of materials such as ceramics, thermosets, carbon, and the like (all of which may be solid or hollow, expanded or expandable) and the like.

One or more thixotropic agents (also sometimes referred to as rheology control agents) are also included in the thermosettable composition, especially where the epoxy resins used are liquid or semi-solid at room temperature or where other liquid components such as reactive diluents and the like are present.

In one embodiment of the invention, the thermosettable composition is formulated to have the consistency of a pliable dough or putty which at room temperature or a slightly elevated temperature (e.g., less than about 80°C) can be readily formed into a desired shape by extrusion, molding or the like and yet which retains that shape once the forming operation is completed.

In another embodiment of the invention, the components of the thermosettable composition and the relative proportions of said components are selected such that the thermosettable composition is pumpable. That is, such thermosettable composition is capable of being pumped into a hollow space or cavity where reinforcement is desired (such, as for example, a pillar, joint or hydroformed part of a vehicle which is otherwise not readily accessible). The thermosettable composition which has been introduced in such manner is thereafter heated (by, for example, placing the vehicle in a paint oven) to a temperature effective to cure and expand the thermosettable composition. Pumping of the thermosettable composition will generally be carried out at a temperature higher than room temperature, but lower than the temperature needed to initiate curing and foaming. It will be desirable to formulate the thermosettable composition such that it is pumpable in the aforescribed manner, yet does not continue to flow after being cooled below the pumping temperature (e.g., to room temperature) or when no longer subjected to a disturbing force such as shear stress.

Manipulation of the viscosity and rheology of the thermosettable composition may be readily accomplished through the use of thixotropic agents. Suitable thixotropic agents include fumed or pyrogenic silica (especially fumed

silica which has been treated with silanes or siloxanes or the like to render it hydrophobic in character), calcium carbonate (especially fine particle coated and/or precipitated calcium carbonate), bentonites, thixotropic clays and the like.

Other optional components include diluents (reactive or non-reactive) such as glycidyl ethers, glycidyl esters, acrylics, solvents and plasticizers, toughening or flexibilizing agents (e.g., aliphatic diepoxides, polyaminoamides, liquid polysulfide polymers), adhesion promoters, colorants (e.g., dyes and pigments such as carbon black), stabilizers (e.g., antioxidants, UV stabilizers) and the like. It is preferred that the thermosettable composition be essentially free of surfactants, as such substances tend to increase the rate at which water can penetrate the thermoset and corrode the surface of a metal substrate to which the thermoset is adhered.

It is particularly advantageous to include one or more rubbers in the thermosettable composition, as such additives will toughen the thermoset and reduce the tendency of the thermoset to crack under stress. As used herein, the term "rubbers" includes both rubbers and elastomers. Suitable rubbers include thermoplastic as well as thermosettable (reactive) rubbers. Illustrative types of rubber include styrene – butadiene rubbers (SBR), nitrile – butadiene rubbers, butyl rubbers, polyisoprene, natural rubber, polybutadiene, chlorobutyl rubbers (neoprene), isobutylene polymers, alpha – olefin elastomers, ethylene – propylene elastomers, chlorosulfonated polyethylenes, ethylene – propylene – diene (EPDM) rubbers, and the like. Thermoplastic block copolymers are one particularly preferred class of rubbers for use in the present invention. Such materials contain one or more base segments ("A") covalently bonded to one or more soft or elastomeric segments ("B"). The A segments may be polystyrene, poly (alpha – methylstyrene), polyethylene, polyurethane, polysulfone, polyester, polycarbonate or the like. The B segments may be polybutadiene, polyisoprene, poly (ethylene – cobutylene), polydimethylsiloxane, polyether, or the like. The block copolymers may have a linear, branched, radial or star structure and may, for example, correspond to the general structure A-B-A, (A-B)_n, and so forth. SIS, SEBS and SBS block copolymers are examples of specific types of such materials. Liquid rubbers, which may be functionalized with carboxy groups, amine groups, or other groups capable of reacting with other components of the thermosettable

composition may also be employed. The use of liquid nitrile rubbers, such as butadiene-acrylonitrile copolymers, is especially desirable.

To improve the corrosion resistance of the composite, the thermosettable composition may additionally include one or more coupling agents and/or metal-modified inorganic oxides. Suitable coupling agents include silanes and organometallates such as organic titanates and zirconates. Organic titanates and zirconates are well known in the art and are described, for example, in U.S. Pat. No. 6,103,784, which is incorporated herein by reference in its entirety. Suitable metal-modified inorganic oxides include alkaline earth metal-modified silicates, for example, calcium ion exchanged amorphous silica gels such as the SHIELDDEX products available from the Grace Davison Division of W.R. Grace.

The relative amounts of the above-described components may, in particular embodiments of the invention, correspond to the following ranges:

15

<u>Component</u>	<u>Preferred (wt%)</u>	<u>More Preferred (wt%)</u>
Epoxy Resin (s)	about 30 to about 75	about 40 to about 65
Rubber(s)	0 to about 20	about 5 to about 15
Boron Trihalide	about 0.2 to about 5	about 0.5 to about 3.5
Amine Adduct(s)		
Hollow Glass	about 1 to about 50	about 10 to about 40
Microspheres		
Filler(s)	0 to about 20	about 10 to about 15
Blowing Agent(s)	about 0.1 to about 5	about 0.2 to about 4
Thixotropic Agent(s)	about 0.1 to about 5	about 1 to about 3
Coupling Agent(s)	0 to about 3	about 0.5 to about 1.5
Metal-Modified	0 to about 5	about 1 to about 3
Inorganic Oxides		

The thermosettable compositions of the present invention can be readily prepared by simply mixing the individual components in desired proportions using

planetary mixers, kneaders, rollers, or the like. The various components are adjusted such that the thermosettable composition retains a workable consistency (i.e. does not cross – link or cure to an unacceptable degree) for at least 1 week at 55°C and at least 1 day at 80°C and does not expand in volume or decrease in specific gravity under such conditions to an unacceptable extent, yet foams and cures within about 10 minutes upon being exposed to a temperature within the range of about 120°C to about 135°C. It is also desirable that the composition exhibits no appreciable deterioration in performance (e.g. % expansion, cured thermoset physical properties such as lap shear or compressive strength) after being exposed to such conditions.

The thermosettable compositions of the present invention may be utilized in any end-use application where an adhesive, sealant or coating is required. However, the thermosettable compositions are especially useful in the production of automobiles and other vehicles to maintain or increase the strength of structural members such as rails, rockers, torsion bars, pillars, radiator support beams, doors, reinforcing beams and the like. The use of structural reinforcement foams in such applications is described, for example, in U.S. Pat. Nos. 4,901,500; 4,751,249; 4,978,562; 4,995,545; 5,124,186; 5,575,526; 5,755,486; 4,923,902; 4,922,596; 4,861,097; 4,732,806; 4,695,343; 4,610,836; 6,068,424; 6,058,673; 6,003,274; 5,992,923; 5,888,600; 6,092,864; 6,079,180; 6,096,403 and 5,884,960 (each of which is incorporated herein by reference in its entirety).

EXAMPLES

Illustrative thermosettable compositions in accordance with the present invention are described in Tables I and I

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TABLE I

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
Epoxy Resin ¹	62.9	60.9	54.4	54.2	53.9	54.1	54.2	54.4	53.8	53.8	53.8
Blowing Agent ²	1.8	1.8	1.8	1.9	1.9	1.9	1.9	1.9	1.8	1.8	1.8
Curative ³	3.0	2.9	2.3	1.7	1.4	1.2	0.9	0.6	1.7	1.4	1.4
Hollow Glass Microspheres ⁴	23.0	22.2	25.2	25.7	25.5	25.6	25.7	25.7	25.4	25.5	25.4
Thixotropic Agent ⁵	3.4	3.3	2.3	2.0	2.9	2.9	2.9	2.9	2.9	2.9	2.9
Rubber ⁶	5.4	5.2	4.7	4.7	4.6	4.6	4.7	4.7	4.6	4.6	4.6
Colorant ⁷	0.1	0.1	---	---	---	---	---	---	---	---	---
Fiber ⁸	---	---	5.3	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8
Alkaline Earth Metal-Modified Silicate ⁹	---	3.3	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Accelerator ¹⁰	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Coupling Agent ¹¹	---	---	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.5

¹ PEP 6134 epoxy resin, a product of Peninsula Polymers² CELOGEN AZ 120 azodicarbonamide blowing agent, a product of Air Products³ DY9577 boron trichloride amine adduct, a product of Ciba-Geigy Corporation⁴ SCOTCHLITE VS 5500 hollow glass microspheres, a product of Minnesota Mining & Manufacturing⁵ CAB-O-SIL TS720 hydrophobic fumed silica, a product of Cabot⁶ NIPOL 1312 liquid nitrile rubber, a product of Zeon⁷ carbon black⁸ glass fiber⁹ SHIELDDEX calcium ion exchanged amorphous silica, a product of the Grace Davison Division of W. R. Grace¹⁰ BIKOT urea accelerator, a product of Uniroyal¹¹ KEN-REACT KR55 titanate, a product of Kenrich Petrochemicals

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TABLE II

	Ex. 12	Ex. 13	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
Epoxy Resin ¹	54.0	54.0	55.0	55.0	55.0	46.5	46.1
Blowing Agent A ²	1.9	1.9	1.9	1.9	1.9	---	---
Blowing Agent B ³	---	---	---	---	---	1.7	1.7
Curative A ⁴	1.7	1.7	1.8	1.8	1.8	---	---
Curative B ⁵	---	---	---	---	0.6	---	0.7
Curative C ⁶	---	---	---	---	---	2.4	2.4
Hollow Glass Microspheres ⁷	25.7	26.0	26.4	27.0	25.8	20.3	20.1
Thixotropic Agent ⁸	2.0	2.9	2.9	2.9	2.9	1.9	1.9
Rubber ⁹	4.7	4.7	4.7	4.7	4.7	12.1	12.0
Fiber ¹⁰	5.8	5.8	5.9	5.9	5.9	12.1	12.0
Alkaline Earth Metal-Modified Silicate ¹¹	3.5	2.3	1.5	0.9	1.5	2.2	2.2
Accelerator ¹²	0.2	0.2	0.2	0.2	0.2	---	---
Titanate A ¹³	0.2	0.2	0.2	0.2	0.2	0.41	0.41
Zirconate B ¹⁴	---	---	---	---	---	0.12	0.12
Titanate C ¹⁵	---	---	---	---	---	0.36	0.36

¹ PEP 6134 epoxy resin, a product of Peninsula Polymers² CELOGEN AZ 120 azodicarbonamide blowing agent, a product of Air Products³ EXPANCEL 051 DU expandable microspheres, a product of Akzo Nobel AB⁴ DY9577 boron trichloride amine adduct, a product of Ciba-Geigy Corporation⁵ AMICURE CG140 dicyandiamide, a product of Air Products⁶ BC120 boron trichloride amine adduct, a product of CVC Specialty Chemicals⁷ SCOTCHLITE VS 5500 hollow glass microspheres, a product of Minnesota Mining & Manufacturing⁸ CAB-O-SIL TS720 hydrophobic fumed silica, a product of Cabot⁹ NIPOL 1312 liquid nitrile rubber, a product of Zeon¹⁰ glass fiber¹¹ SHIELDDEX calcium ion exchanged amorphous silica, a product of the Grace Davison Division of W.R. Grace¹² BIKOT urea accelerator, a product of Uniroyal¹³ KEN-REACT KR55 titanate, a product of Kenrich Petrochemicals¹⁴ KEN-REACT NZ97 zirconate, a product of Kenrich Petrochemicals¹⁵ KEN-REACT KR238M titanate, a product of Kenrich Petrochemicals

What is claimed is:

1. A thermosettable composition comprising:
 - 5 (a) at least one epoxy resin;
 - (b) at least one blowing agent;
 - (c) at least one curative selected from the group consisting of boron trihalide amine adducts;
 - (d) hollow glass microspheres; and
 - 10 (e) at least one thixotropic agent

wherein said thermosettable composition is stable at 55°C for at least 1 week and at 80°C for at least 1 day and cures and foams upon being exposed to a temperature in the range of about 120°C to about 135°C.
2. The thermosettable composition of claim 1 wherein said thermosettable composition is pumpable at 80°C.
3. The thermosettable composition of claim 2 wherein said thermosettable composition has the consistency of a pliable dough at room temperature.
4. The thermosettable composition of claim 1 wherein at least one epoxy resin is a polyglycidyl ether of a polyhydric phenol.
- 20 5. The thermosettable composition of claim 1 wherein at least one blowing agent is selected from the group consisting of azo compounds and physical blowing agents encapsulated in thermoplastic shells.
6. The thermoplastic composition of claim 1 wherein boron trihalide amine adduct is present in the thermosettable composition at a concentration of
- 25 from about 0.5 to about 5 weight percent.
7. The thermosettable composition of claim 1 wherein one or more boron trichloride amine adducts are the sole curatives present in the thermosettable composition.
8. The thermosettable composition of claim 1 wherein the hollow glass microspheres have a crush strength of at least about 200 Kg/cm² and
- 30 diameters in the range of from about 5 to about 200 micrometers.
9. The thermosettable composition of claim 1 wherein at least one thixotropic agent is fumed silica.

10. The thermosettable composition of claim 1 additionally comprising reinforcing fibers.
11. The thermosettable composition of claim 10 wherein the reinforcing fibers are selected from the group consisting of glass fibers, wollastonite fibers, polyaramid fibers and combinations thereof.
12. The thermosettable composition of claim 1 additionally comprising at least one rubber.
13. The thermosettable compositions of claim 12 wherein at least one rubber is a liquid nitrile rubber.
14. The thermosettable composition of claim 1 additionally comprising at least one guanidine curative.
15. The thermosettable composition of claim 14 wherein at least one guanidine curative is dicyandiamide.
16. The thermosettable composition of claim 1 additionally comprising at least one anti-corrosion agent selected from the group consisting of silanes, titanates, zirconates, and alkaline earth metal-modified silicates.
17. A structural foam obtained by heating the thermosettable composition of claim 1.
18. A composite comprised of a solid article and the structural foam of claim 17.
19. A preform part useful for reinforcing a structural member, said preform part comprising a carrier and the thermosettable composition of claim 1.
20. A thermosettable composition comprising:
 - (a) from about 30 to about 75 wt % of one or more epoxy resins;
 - (b) from about 0.1 to about 5 wt % of one or more blowing agents;
 - (c) from about 0.2 to about 5 wt % of one or more boron trichloride amine adducts;
 - (d) from about 1 to about 50 wt % hollow glass microspheres;
 - (e) from about 0.1 to about 5 wt % of one or more thixotropic agents;wherein said thermosettable composition is stable at 55°C for at least 1 week and at 80°C for at least 1 day and cures and foams upon being exposed to a temperature in the range of about 120°C to about 135°C.
21. A structural foam obtained by heating the thermosettable composition of claim 20.

22. A composite comprised of a solid article having at least one surface and the structural foam of claim 21 adhered to said at least one surface of the solid article.
23. A preform part useful for reinforcing a structural member having a cavity therein, said preform part comprising a carrier and the thermosettable composition of claim 20 and being of a size and configuration capable of fitting inside said cavity.
24. A thermosettable composition comprising:
- (a) from about 40 to about 65 wt % of one or more polyglycidyl ethers of one or more polyhydric phenols;
 - (b) from about 0.2 to about 4 wt % of one or more blowing agents selected from the group consisting of azo compounds and physical blowing agents encapsulated in thermoplastic shells;
 - (c) from about 0.5 to about 3.5 wt % of one or more boron trichloride amine adducts;
 - (d) from about 10 to about 40 wt % of hollow glass microspheres having a crush strength of at least 3000 psi;
 - (e) from about 0.5 to about 1.5 wt % of hydrophobic fumed silica;
- wherein said thermosettable composition is stable at 55°C for at least 1 week and at 80°C for at least 1 day and cures and foams upon being exposed to a temperature in the range of about 120°C to about 135°C.
25. A structural foam obtained by heating the thermosettable composition of claim 24.
26. A composite comprised of a solid article having at least one surface and the structural foam of claim 25 adhered to said at least one surface of the solid article.
27. A preform part useful for reinforcing a structural member having a cavity therein, said preform part comprising a carrier and the thermosettable composition of claim 24 and having a size and configuration capable of fitting inside said cavity.
28. A method of reinforcing a structural member having a cavity therein, said method comprising introducing a quantity of the thermosettable composition of claim 24 into said cavity and heating the thermosettable composition at a

temperature of at least about 120°C for a time effective to initiate foaming and curing of said quantity of thermosettable composition.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/45000

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : B32B 5/22, 3/26; C08J 9/00

US CL : 428/ 308.4, 317.9, 319.1; 521/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/ 308.4, 317.9, 319.1; 521/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, E	US 6,332,731 B1 (WYCECH) 25 December 2001, the whole document.	1-15, 17-28
Y	US 6,237,304 B1 (WYCECH) 29 May 2001, the whole document.	1-15, 17-28
Y	US 6,233,826 B1 (WYCECH) 22 May 2001, the whole document.	1-15, 17-28
Y	US 6,103,784 A (HILBORN et al) 15 August 2000, abstract.	16
Y	US 3,395,121 A (PFANN et al) 30 July 1968, column 2, lines 3-44.	1-15, 17-28

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

Special categories of cited documents:	
A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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O document referring to an oral disclosure, use, exhibition or other means	*&* document member of the same patent family
P document published prior to the international filing date but later than the priority date claimed	

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18 APR 2002

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